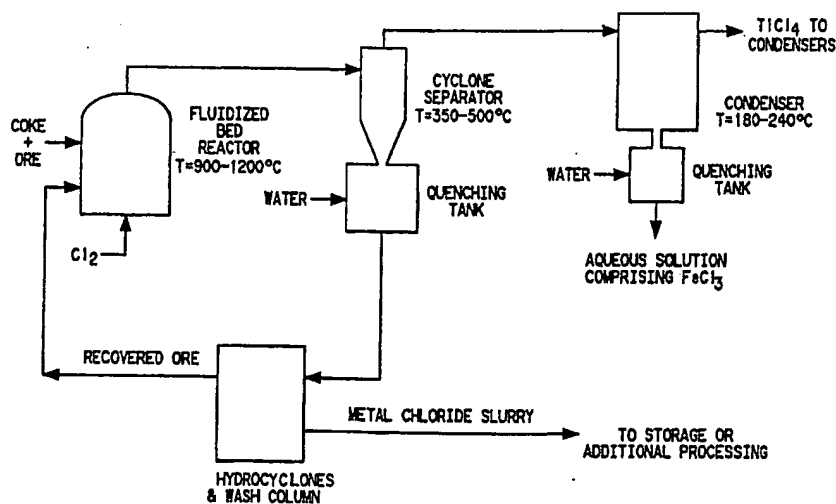




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(54) Title: A PROCESS FOR PRODUCING AN AQUEOUS SOLUTION COMPRISING FERRIC CHLORIDE



(57) Abstract

The present invention provides a process for preparing an aqueous solution of FeCl_3 . The process involves the steps of: (a) reacting an ore material comprising titanium and iron with chlorine and coke to form a metal chloride vapor stream comprising titanium tetrachloride, ferrous chloride, ferric chloride and unreacted coke and ore solids; (b) cooling the metal chloride vapor stream to a temperature in the range of 350 to 500 °C to condense at least some of the ferrous chloride; (c) separating the condensed ferrous chloride and the unreacted coke and ore solids from the metal chloride vapor stream; (d) cooling the metal chloride vapor stream to a temperature in the range of 180 to 240 °C to form a precipitate comprising ferric chloride; and (e) adding the precipitate to water to form an aqueous solution comprising ferric chloride. The resulting aqueous solution has a high FeCl_3 content, and can be used in wastewater treatment applications.

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TITLE

5 A PROCESS FOR PRODUCING AN AQUEOUS SOLUTION
 COMPRISING FERRIC CHLORIDE

BACKGROUND OF THE INVENTION

10

Field of the Invention

 The present invention relates to a process for preparing an aqueous solution
comprising ferric chloride. The ferric chloride is produced from the chlorination of
15 titanium-bearing materials.

Description of the Related Art

 Large amounts of metal chlorides arise as by-products from various industrial
20 processes. For example, in a chloride process for making titanium dioxide (TiO_2)
pigment, titanium-bearing material or ore is chlorinated to produce titanium tetrachloride
(TiCl_4) and other metal chloride by-products. The metal chloride by-products are highly
acidic and often contain iron chlorides as a major ingredient. Many processes to treat
these materials are expensive and produce a product that must be disposed of by
25 neutralization, landfilling, deepwelling, or other disposal methods.

 The need therefore exists for a process for treating aqueous media containing
metal chlorides that provides non-hazardous products that can be used in commercial
applications.

It is known that iron chloride can be used as a flocculant for treatment of waste water. Conventionally high purity iron chloride solutions have been utilized for this purpose. Tedious and expensive processes have been developed to purify metal chloride
5 by-product streams to render them suitable for use to treat wastewater.

Cairns and Kleinfelder, U. S. Patent 3,261,664 describe a process to remove ferrous chloride (FeCl_2) from hot gases containing ferric chloride (FeCl_3), TiCl_4 , and blowover solids comprising unreacted ores and carbon-containing material from a reaction
10 for the chlorination of titanium-bearing materials which involves the following steps: (a) passing a stream containing FeCl_2 , FeCl_3 and TiCl_4 into a flue at 900°C ; (b) injecting cool TiCl_4 into the flue to cool the stream to $500\text{--}550^\circ\text{C}$ which condenses FeCl_2 as a solid; (c) passing the mixture containing solid FeCl_2 and remaining gases to a dust or cyclone-type separator to separate solid FeCl_2 and blowover solids from the gases; (d) passing the gases
15 to cooling towers, wherein FeCl_3 is removed by conventional means, e. g., by cooling the gases to $250\text{--}270^\circ\text{C}$ by a shower of an inert cooling medium such as cool TiCl_4 , to form solid FeCl_3 ; (e) passing the mixture containing gases and solid FeCl_3 to a cyclone separator to remove solid FeCl_3 ; (f) condensing the remaining gases which are now free of solid chlorides; and (g) recovering liquid TiCl_4 .

20 Rado and Nelson, U. S. Patent 3,906,077 disclose a process for recovering substantially pure FeCl_3 from chlorinating an iron-containing ore which includes separation of a major portion of non-volatile solids in a first cyclone, followed by a cooling step (addition of liquid TiCl_4), to precipitate FeCl_3 , use of a second cyclone to separate FeCl_3
25 and all other remaining non-volatile solids, and purification of FeCl_3 by recovery as overhead from a treatment zone at $350\text{--}700^\circ\text{C}$.

Hartmann and Schmeir, U. S. Patent 5,248,497 disclose a process for the recovery of ferrous chloride from the gaseous effluent resulting from chlorination of titanium-

containing material which involves: (a) separating FeCl_2 and blowover solids (unreacted coke, ore) and other metal chlorides in a cyclone to form cyclone dust; (b) slurrying the cyclone dust with a liquid (water, HCl); (c) removing the water-insoluble constituents of the slurry e. g., by filtration; (d) evaporating the solution under vacuum; (e) cooling the evaporated solution to allow FeCl_2 to crystallize; and (f) separating the FeCl_2 crystals. This patent does not describe a process for separating FeCl_3 or a process to provide a solution of FeCl_3 having low solids content.

Heretofore, a process where titanium-containing material is chlorinated to produce a metal chloride vapor stream which is cooled to a temperature greater than 500°C to condense out a fraction of the FeCl_2 and other metal chlorides having high boiling points such as lead chloride (PbCl_2), manganese chloride (MnCl_2), magnesium chloride (MgCl_2), and chromium chloride (CrCl_3) in a cyclone separator has been commercially practiced. The precipitated solids as well as most of the entrained coke, ore, and gangue solids are collected in the cyclone underflow, thus purifying the FeCl_3 vapor stream which exits in the cyclone overflow.

In this commercial process, the cyclone overflow is further cooled to $180\text{--}240^\circ\text{C}$, wherein FeCl_3 is precipitated and then slurried with water to form an aqueous solution of FeCl_3 containing dissolved FeCl_2 and other miscellaneous metal chlorides, and trace amounts of water-insoluble coke, ore, and gangue solids. The FeCl_3 solution is further processed through a screening/settling process to reduce solids concentration to provide a product suitable for wastewater treatment applications.

Although the above-described process is effective in producing an aqueous solution of FeCl_3 , it would be desirable to have an improved process which removes a larger fraction of the chlorides having high boiling point temperatures from the FeCl_3 stream. Also, when the above-described process is operated, solids build up on

downstream piping and equipment causing restrictions and pluggage. Thus, it would be desirable to have a process which could be run more continuously with fewer downstream restrictions and pluggage.

5

The present invention provides an improved process which can be operated more continuously with fewer pluggage and restriction problems. The resulting aqueous solution has a high iron content, particularly a high FeCl_3 content, while having a low chromium chloride content, which is advantageous in wastewater treatment applications.

10

SUMMARY OF THE INVENTION

The present invention provides a process for preparing an aqueous FeCl_3 solution, comprising the steps of: (a) reacting an ore material comprising titanium and iron with chlorine and coke to form a metal chloride vapor stream comprising titanium tetrachloride, ferrous chloride, ferric chloride and unreacted coke and ore solids; (b) cooling the metal chloride vapor stream to a temperature in the range of 350 to 500°C to condense at least some of the ferrous chloride; (c) separating the condensed ferrous chloride and the unreacted coke and ore solids from the metal chloride vapor stream; (d) cooling the metal chloride vapor stream to a temperature in the range of 180 to 240°C to form a precipitate comprising ferric chloride; and (e) adding the precipitate to water to form an aqueous solution comprising ferric chloride.

25

In addition to ferrous chloride, other metal chlorides having a boiling point higher than the cooling temperature are condensed in the above-described step (b) and removed from the metal chloride stream in the above-described step (c). Examples of such metal chlorides include chromium chloride, manganese chloride, magnesium chloride, lead chloride, and mixtures thereof. The metal chloride stream is preferably cooled in step (b)

by injection of liquid titanium tetrachloride and the condensed solids are preferably removed in step (c) using a cyclone. The ferrous chloride and other metal chlorides can be removed from the cyclone through any suitable conveying device, preferably a rotary
5 valve. Typically, the ferrous chloride and other metal chlorides are separated and removed from the metal chloride vapor stream in step (c) and conveyed to a quenching tank containing water.

Typically, the precipitate comprising the ferric chloride formed in the above-
10 described step (d) is conveyed to a quenching tank containing water. The metal chloride stream is preferably cooled by addition of liquid titanium tetrachloride in step (d).

Typically, the aqueous ferric chloride solution formed by the process of this invention comprises some ferrous chloride. Chlorine may be injected into the solution to
15 convert at least some of the ferrous chloride to ferric chloride. Preferably, the aqueous solution comprises 1-45%, more preferably 30-45%, by weight of ferric chloride, less than 0.5% by weight of ferrous chloride, less than 1% by weight of hydrochloric acid, and less than 0.5% by weight of solids based on total weight of the solution. Additional processing to remove at least some of the solids can also be performed.

20

BRIEF DESCRIPTION OF THE FIGURE

Figure 1 is a schematic diagram showing a preferred embodiment of the process of
25 this invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for preparing an aqueous solution
5 comprising ferric chloride.

In the process of the present invention, a titanium- and iron-containing ore
material, a carbonaceous material or coke, chlorine, and optionally air or oxygen are fed
into a fluidized bed reactor, where they react to provide a metal chloride vapor stream
10 comprising titanium tetrachloride, ferrous chloride, ferric chloride, other metal chlorides,
CO₂, CO, and solid particulates comprised of unreacted ore, coke and gangue. The
titanium-containing material can be any suitable titanium source material such as titanium-
containing ores including rutile, ilmenite or anatase ore; beneficiates thereof; titanium-
containing by-products or slags; and mixtures thereof and typically contain iron as a major
15 ingredient. Reactor conditions are preferably maintained to convert the iron-containing
material to ferric chloride.

The metal chloride vapor stream from the fluidized bed reactor is then cooled to a
temperature in the range of 350 to 500°C and directed to a gas-solid separation device,
20 preferably a cyclone. The metal chloride vapor stream may be cooled by any suitable
means, for example, an inert liquid coolant, preferably liquid titanium tetrachloride (TiCl₄),
may be injected into the stream upstream of the cyclone to control the temperature at the
inlet to the cyclone.

25 Generally, the temperature of the cyclone determines which metal chlorides will
condense as solids (or liquids). Metal chlorides having boiling points higher than the
cyclone temperature will condense and precipitate, e. g., ferrous chloride (FeCl₂);
chromium chloride (CrCl₃); manganese chloride (MnCl₂); magnesium chloride (MgCl₂),
and lead chloride (PbCl₂), and mixtures thereof. Most of the condensed metal chlorides

are collected in the cyclone underflow. Most of the unreacted coke, ore and gangue solids and lesser amounts of FeCl_3 are also collected in the cyclone underflow.

5 As discussed above, in conventional processes, the cyclone is operated at an inlet temperature (cooling temperature) higher than 500°C to prevent liquid FeCl_3 from condensing out of the stream and causing plugging problems. Surprisingly, it has now been found that when the metal chloride vapor stream is cooled to a temperature in the range of 350 to 500°C at the cyclone inlet, the process is less prone to pluggage in piping
10 and equipment downstream of the cyclone, while being more effective in separating and removing a significant portion of FeCl_2 and other metal chlorides from the vapor stream. The process of this invention can be run more continuously, with fewer restrictions and less pluggage than observed in conventional processes.

15 In the present invention, a maximum temperature of 500°C is significant, because at cyclone inlet temperatures higher than 500°C , the metal chlorides having high boiling points (e.g., FeCl_2) are less efficiently removed from the vapor stream in the cyclone. While not wishing to be bound by any theory, it is believed that pluggage in piping and equipment downstream of the cyclone can be caused by either condensation of ferrous
20 chloride and other high-boiling chlorides or condensation of ferric chloride. Operating below 500°C reduces pluggage by decreasing the amount of condensation of ferrous chloride and other high boiling chlorides in piping and equipment downstream of the cyclone. A minimum temperature of 350°C is also significant, because at temperatures lower than 350°C , liquid FeCl_3 which has a relatively low boiling point may condense in
25 the same piping and equipment, or even in the cyclone, causing pluggage. To optimize removal of CrCl_3 , MnCl_2 , MgCl_2 , PbCl_2 and other metal chlorides having high boiling points with minimal loss of FeCl_3 and minimal pluggage, the preferred cyclone inlet temperature is 375 - 475°C and most preferably 400 - 450°C .

The solids in the cyclone underflow are conveyed into a quenching tank where they are dissolved and slurried into water. A number of suitable conveying devices can be used in the process of this invention, but it is preferred to use a rotary valve.

5

Optionally, the cyclone underflow solids can be slurried with water to form an aqueous slurry of dissolved metal chlorides and ore, coke, and gangue solids. The cyclone underflow slurry can be processed through hydrocyclone separators and a wash column to recover some of the ore which is recycled to the fluidized-bed reactor.

10

The metal chloride vapor stream exiting the cyclone overflow is further cooled to 180-240°C by addition of a liquid coolant, such as liquid TiCl_4 . Ferric chloride is precipitated and collected as a solid along with any remaining ferrous chloride, coke, ore, and gangue solids. Any suitable gas-solid separation device can be used. The solids are dissolved and slurried with water to form an aqueous solution of ferric chloride containing trace amounts of coke, ore and gangue solids. Optionally, the aqueous solution can be treated with chlorine, for example, in a plug flow reactor to convert at least some of the ferrous chloride to ferric chloride. After such chlorine treatment, there is preferably less than 0.5% by weight ferrous chloride in solution.

15

20

The product of this invention comprising an aqueous solution of ferric chloride can be used in water treatment directly without additional processing. Preferably, this solution has the following composition:

5	FeCl_3	1-45 wt%, preferably 30-45 wt%
	FeCl_2	< 0.5 wt%
	HCl	<1 wt%
	Suspended solids	< 0.5 wt.% (coke, ore, gangue)
	Other metal chlorides*	< 4000 ppm
10	Balance is water.	

*Concentration of other metal chlorides will depend on their concentrations in the titanium- and iron-containing ore feed.

15 Additional removal of solids can be optionally performed by various solids removal techniques including using a settling pond, filter press, centrifuge, or flotation process. Such additional steps can reduce solids concentrations to less than 0.2 wt.%, typically less than 0.1 wt.%. Further, chlorination of the aqueous solution to lower concentrations of ferrous chloride can also be performed after the additional solids-removal step.

20

A preferred embodiment of the process of this invention is shown in Figure 1.

After removal of the ferric chloride and remaining coke and ore solids, the metal chloride vapor stream comprises titanium tetrachloride (TiCl_4) and is fed to additional
25 equipment downstream where purified liquid TiCl_4 is produced which is used as a feed for TiO_2 pigment production.

The present invention provides a process to prepare an aqueous solution comprising ferric chloride which has practical use as a wastewater treatment agent. Ferric

chloride is used for reduction of total suspended solids (TSS), biochemical oxygen demand, chemical oxygen demand, phosphorus, color, trace metals and odor as well as sludge conditioning. For example, ferric chloride aids in removal of TSS in wastewater by
5 forming a hydroxide gel which coagulates fine particles into larger agglomerates which can be removed in standard separation equipment.

The invention is further illustrated by the following examples, but these examples should not be construed as limiting the scope of the invention.

10

EXAMPLE 1

A mixture of 60 wt% ilmenite and 40 wt% titanium-containing slag (mixture
15 composition of 71% TiO_2 , 24% Fe_2O_3 , 5% other metal oxides) was reacted with petroleum coke and chlorine gas in a fluidized-bed reactor at a temperature of 1000-1200°C. Reactor conditions were maintained so that the Fe_2O_3 was preferentially converted to FeCl_3 with the remainder converted to FeCl_2 ($\text{Fe}^{3+}/\text{Fe} = 0.70\text{-}0.80$).

20 The chlorination reactor outlet stream was cooled to approximately 500°C by injecting liquid TiCl_4 into the flue just upstream of the cyclone inlet to condense ferrous chloride and other metal chlorides having a boiling point higher than 500°C. The condensed metal chloride solids as well as entrained ore and coke particles were collected in the cyclone. The solids underflow temperature measured at the bottom of the cyclone
25 was 325°C. Cyclone collection efficiencies for the various components under these conditions are given in Table 1.

The solids in the cyclone underflow were conveyed by a rotary valve into a quenching tank where the solids were dissolved and slurried into water. The cyclone

underflow slurry was pumped to hydrocyclone separators and a wash column to recover some of the ore which was recycled to the chlorination reactor.

5 The vapor stream exiting the cyclone entered a condenser where liquid TiCl_4 was injected to cool the stream to 210°C to condense FeCl_3 . TiCl_4 remained as a vapor and exited the condenser overhead to additional condensing equipment downstream where the TiCl_4 vapor was condensed and collected.

10 FeCl_3 and other precipitated metal chlorides were collected in the condenser. The solids in the condenser underflow were conveyed into a quenching tank where they were dissolved and slurried into water. The composition of the aqueous FeCl_3 solution thus produced is given in Table 2.

15

Table 1

Collection Efficiencies (wt. %) of Cyclone Separator for Example 1
(Inlet Temperature = 500°C , Solids Underflow Temperature = 325°C)

20

Cr	71
Mn	68
Mg	70
Pb	31
25 FeCl ₃	1.1
FeCl ₂	71
Ore + Gangue	93
Coke	95

Table 2**Composition of Aqueous FeCl₃ Solution Produced in Example 1**

5

FeCl ₃	36 wt%
FeCl ₂	1.9 wt%
Free HCl	<1.0 wt%
Suspended Solids	0.17 wt%
10 Cr*	85 ppm
Mn*	2500 ppm
Mg*	520 ppm
Pb*	100 ppm

15 *Concentration of miscellaneous metals will depend on their concentrations in the titanium- and iron-containing ore feed.

EXAMPLE 2

20

A mixture of 75 wt% ilmenite and 25 wt% titanium-containing slag (mixture composition of 71% TiO₂, 25% Fe₂O₃, 4% other metal oxides) was reacted with petroleum coke and chlorine gas in a fluidized-bed reactor at a temperature of 1000-1200°C. Reactor conditions were maintained so that the Fe₂O₃ was preferentially
25 converted to FeCl₃ with the remainder converted to FeCl₂ (Fe³⁺/Fe = 0.70-0.80).

The chlorination reactor outlet stream was cooled to approximately 400°C by injecting liquid TiCl₄ into the flue just upstream of the cyclone inlet to condense ferrous chloride and other metal chlorides having a boiling point higher than 400°C. The

condensed metal chloride solids as well as entrained ore and coke particles were collected in the cyclone. The solids underflow temperature measured at the bottom of the cyclone was 260°C. Cyclone collection efficiencies for the various components under these
5 conditions are given in Table 3.

The solids in the cyclone underflow were conveyed by a rotary valve into a quenching tank where the solids were dissolved and slurried into water. The cyclone underflow slurry was pumped to hydrocyclone separators and a wash column to recover
10 some of the ore which was recycled to the chlorination reactor.

The vapor stream exiting the cyclone entered a condenser where liquid TiCl_4 was injected to cool the stream to 210°C to condense FeCl_3 . TiCl_4 remained as a vapor and exited the condenser overhead to additional condensing equipment downstream where the
15 TiCl_4 vapor was condensed and collected.

FeCl_3 and other precipitated metal chlorides were collected in the condenser. The solids in the condenser underflow were conveyed into a quenching tank where they were dissolved and slurried into water. The composition of the aqueous FeCl_3 solution thus
20 produced is given in Table 4.

Table 3**Collection Efficiencies (wt. %) of Cyclone Separator for Example 2****(Inlet Temperature = 400°C, Solids Underflow Temperature = 260°C)**

5	Cr	95
	Mn	95
	Mg	95
10	Pb	69
	FeCl ₃	4
	FeCl ₂	86
	Ore + Gangue	99
	Coke	93

15

Table 4**Composition of Aqueous FeCl₃ Solution Produced in Example 2**

	FeCl ₃	40 wt%
20	FeCl ₂	2.2 wt%
	Free HCl	< 1.0 wt%
	Suspended Solids	0.17 wt%
	Cr*	30 ppm
	Mn*	570 ppm
25	Mg*	150 ppm
	Pb*	60 ppm

*Concentration of miscellaneous metals will depend on their concentrations in the titanium- and iron-containing ore feed.

Claims

- 5 1. A process for preparing an aqueous solution comprising ferric chloride, comprising the steps of:
- (a) reacting an ore material comprising titanium and iron with chlorine and coke to form a metal chloride vapor stream comprising titanium tetrachloride, ferrous chloride, ferric chloride and unreacted coke and ore solids;
- 10 (b) cooling the metal chloride vapor stream to a temperature in the range of 350 to 500°C to condense at least some of the ferrous chloride;
- (c) separating the condensed ferrous chloride and the unreacted coke and ore solids from the metal chloride vapor stream;
- (d) cooling the metal chloride vapor stream to a temperature in the range of 180 to
- 15 240°C to form a precipitate comprising ferric chloride; and
- (e) adding the precipitate to water to form an aqueous solution comprising ferric chloride.
2. The process of claim 1, wherein in addition to ferrous chloride, other metal chlorides,
- 20 having a boiling point higher than the cooling temperature are condensed in step (b), and separated and removed from the metal chloride vapor stream in step (c).
3. The process of claim 2, wherein the other metal chlorides are selected from the group consisting of chromium chloride, manganese chloride, magnesium chloride, lead chloride,
- 25 and mixtures thereof.
4. The process of claim 2, wherein the ferrous chloride and other metal chlorides are separated and removed from the metal chloride vapor stream in step (b) and conveyed to a quenching tank containing water.

5. The process of claim 1, wherein the condensed ferrous chloride and the unreacted coke and ore solids are separated from the metal chloride vapor stream by a cyclone in step (c).
- 5 6. The process of claim 1, wherein titanium tetrachloride is added to the metal chloride vapor stream for cooling in steps (b) and (d).
7. The process of claim 1, wherein the precipitate comprising the ferric chloride formed in step (d) is conveyed to a quenching tank containing water.
- 10 8. The process of claim 1, wherein the aqueous solution formed in step (e) comprises ferrous chloride.
9. The process of claim 8, wherein chlorine is injected into the aqueous solution to
15 convert at least some of the ferrous chloride to ferric chloride.
10. The process of claim 1, wherein the aqueous solution comprises 1 to 45% by weight of ferric chloride based on total weight of the solution.
- 20 11. The process of claim 10, wherein the aqueous solution comprises 30 to 45% by weight of ferric chloride based on total weight of the solution.
12. The process of claim 10, wherein the aqueous solution comprises less than 0.5% by weight of ferrous chloride, less than 1% by weight of hydrochloric acid, and less than
25 0.5% by weight of solids based on total weight of the solution.

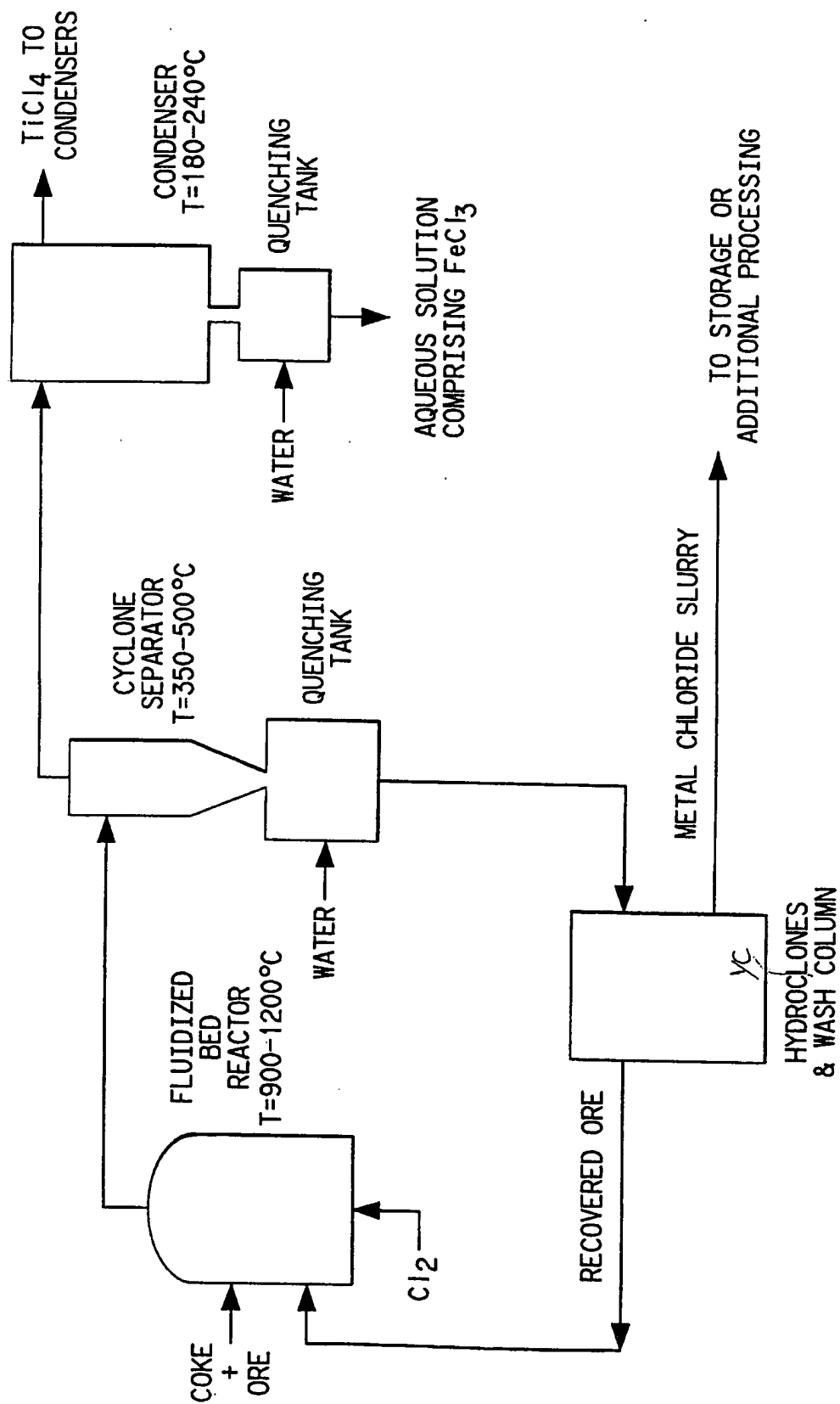


FIG.1

INTERNATIONAL SEARCH REPORT

Inter nal Application No

PCT/US 98/14071

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01G49/10 C22B34/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01G C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 340 071 A (ATOCHEM) 2 November 1989 see the whole document	1,8,9
A	US 4 540 551 A (BONSACK JAMES P ET AL) 10 September 1985	

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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/14071

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